CHAPTER V

CRYSTAL AND MOLECULAR STRUCTURE OF

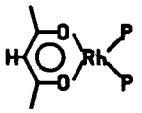
RHODIUM-2,4-PENTADIONATE-BIS(2,2'-BIS(4,6-DI-T-BUTYLPHENYL)PHENYLPHOSPHITE)

5.0 Abstract.

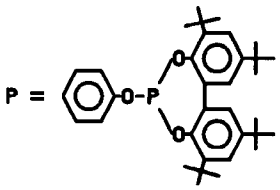
Rhodium-2,4-pentadionate-bis(2,2'-bis(4,6-di-t-butylphenyl)phenyl phosphite) (1), $C_{73}H_{97}O_8P_2Rh(C_7H_8)$, M_r = 1359.56, triclinic, $P\bar{1}$, a = 11.624(1), b = 17.244(2), c = 18.877(1) Å, α = 79.884(8)°, β = 84.812(6)° , γ = 75.398(9)° , V = 3600.4(6) Å^3 , Z = 2, D_x = 1.254 gcm^{-3} , (Mo K$\bar{\alpha}$) = 0.71073 Å, μ = 3.3 cm^{-1}, F(000) = 1448, T = 130 K, R_F = 0.042 for 10706 unique observed reflections with $I \geq 2.5\sigma(I)$ and 1136 parameters. The square planar coordination of the complex is tetrahedrically distorted. The two phosphite ligands of the rhodium-complex are deformed due to sterical interactions.

5.1 Introduction

The hydroformylation of otherwise unreactive internal and branched alkenes can be achieved by using bulky phosphite modified rhodium catalysts[1] . The title compound is a precursor for one of these catalysts and therefore the sterical conformation of this bisphosphite complex is of use in the study of the catalytic cycle of these catalysts. system. The triphenylphosphite analogue (2) of the title compound has been crystallized by Leipoldt et.al.[2]. Other bulky phosphites i.e. tri(2-t-butylphenyl)phosphite[3] (3), tri(2,4,6,-trimethylphenyl)-phosphite[4] (4) and bis(2-t-butyl-6-methylphenyl)phenylphosphite[5] (5) exclusively yielded the monophosphite rhodium complex Rh(acac)(CO)P (acac=2,4-pentadionate, CO=carbonyl and P=phosphite ligand)



(1)



5.2 Experimental.

X-ray diffraction: Crystal and Molecular Structure.

The yellow colored crystal, a parallelepiped of size 0.15 x 0.33 x 0.40 mm., used for characterization and data collection was glued on top of a glass fiber and transferred to the goniostat and cooled to 130 K by using an on-line liquid nitrogen cooling system mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a VAX-11/730 computer. Graphite-monochromated Mo K$\bar{\alpha}$ radia-tion ($\bar{\lambda}$ = 0.71073 Å) used to obtain 14851 reflections (h 0 → 14, k -20 → 20, l -23 → 23); 1.13° < θ < 26.0°; $[(\sin\theta)]_{max}/\lambda$ = 0.6168 $Å^{-1}$; $\omega/2\theta$] scan, $\Delta\omega$ = (0.70 + 0.34n tg θ)°. Unit cell parameters with their standard deviations and orientation matrix were determined from a least-squares treatment of the SET4[6] setting angles of 22 reflections with 14.84 < θ < 18.83° . The unit cell was identified as triclinic, space group $P\bar{1}$. This choice was

Atoms of the Asymmetric Unit.	x	y	z	s.o.f.	U_{eq} $(Å^2)$*
Residue 1.					
Rh(1)	.24589(2)	.25048(2)	.25092(1)	1.0(-)	.0167(1)
P(1)	.33686(7)	.29811(5)	.32160(4)	1.0(-)	.0160(2)
P(2)	.39402(7)	.20136(5)	.18155(4)	1.0(-)	.0181(2)
O(1)	.09006(19)	.30273(14)	.30461(12)	1.0(-)	.0270(8)
O(2)	.1490(2)	.19744(14)	.19480(12)	1.0(-)	.0284(8)
O(3)	.30218(17)	.39500(12)	.32417(10)	1.0(-)	.0169(6)
O(4)	.48010(17)	.27538(12)	.31838(10)	1.0(-)	.0167(6)
O(5)	.30010(19)	.26871(12)	.40434(10)	1.0(-)	.0206(7)
O(6)	.52260(18)	.21956(12)	.18494(10)	1.0(-)	.0173(6)
O(7)	.42558(19)	.10493(12)	.17982(11)	1.0(-)	.0213(7)
O(8)	.3615(2)	.23240(13)	.09835(11)	1.0(-)	.0235(7)
C(1)	-.0135(3)	.2967(2)	.29351(18)	1.0(-)	.0308(11)
C(2)	-.0410(3)	.2478(2)	.2497(2)	1.0(-)	.0330(11)
C(3)	.0390(3)	.2009(2)	.20515(19)	1.0(-)	.0318(12)
C(4)	-.1145(4)	.3488(3)	.3326(2)	1.0(-)	.0504(18)
C(5)	-.0098(5)	.1508(3)	.1629(3)	1.0(-)	.0577(19)
C(6)	.3679(3)	.45048(18)	.29268(15)	1.0(-)	.0161(8)
C(7)	.4822(3)	.44022(17)	.31606(15)	1.0(-)	.0160(9)
C(8)	.5480(3)	.49647(18)	.28499(15)	1.0(-)	.0170(9)
C(9)	.5037(3)	.56079(18)	.23294(15)	1.0(-)	.0176(9)
C(10)	.3852(3)	.57138(19)	.21464(16)	1.0(-)	.0190(9)
C(11)	.3143(3)	.51840(18)	.24363(15)	1.0(-)	.0171(9)
C(12)	.5770(3)	.62082(19)	.19592(16)	1.0(-)	.0207(10)
C(13)	.5271(3)	.7034(2)	.22064(19)	1.0(-)	.0257(11)
C(14)	.7079(3)	.5915(2)	.2139(2)	1.0(-)	.0275(11)
C(15)	.5697(4)	.6315(2)	.11402(18)	1.0(-)	.0295(11)
C(16)	.1840(3)	.53467(19)	.22311(16)	1.0(-)	.0205(9)
C(17)	.1698(3)	.4712(2)	.1796(2)	1.0(-)	.0286(12)
C(18)	.1000(3)	.5355(2)	.2909(2)	1.0(-)	.0304(11)
C(19)	.1432(3)	.6181(2)	.1759(2)	1.0(-)	.0296(11)
C(20)	.5413(2)	.29299(18)	.37240(15)	1.0(-)	.0166(9)
C(21)	.5373(2)	.37358(18)	.37321(15)	1.0(-)	.0155(8)
C(22)	.5945(3)	.39233(18)	.42765(15)	1.0(-)	.0148(8)
C(23)	.6558(3)	.33225(18)	.47912(15)	1.0(-)	.0164(9)
C(24)	.6624(3)	.25153(18)	.47299(16)	1.0(-)	.0180(9)
C(25)	.6078(3)	.22856(18)	.41997(15)	1.0(-)	.0174(9)
C(26)	.7113(3)	.35231(18)	.54281(16)	1.0(-)	.0183(9)
C(27)	.7300(4)	.4384(2)	.5276(2)	1.0(-)	.0290(11)
C(28)	.6248(4)	.3462(2)	.60861(19)	1.0(-)	.0313(11)
C(29)	.8299(3)	.2931(2)	.5603(2)	1.0(-)	.0307(12)
C(30)	.6298(3)	.13875(18)	.41099(17)	1.0(-)	.0234(10)
C(31)	.6996(3)	.0827(2)	.4726(2)	1.0(-)	.0281(11)
C(32)	.5149(4)	.1118(2)	.4088(3)	1.0(-)	.0427(14)
C(33)	.7048(4)	.1274(2)	.3410(2)	1.0(-)	.0384(14)
C(34)	.2576(3)	.31423(18)	.45992(16)	1.0(-)	.0184(9)
C(35)	.1380(3)	.3527(2)	.46415(18)	1.0(-)	.0265(11)
C(36)	.0943(3)	.3924(2)	.52235(19)	1.0(-)	.0283(11)
C(37)	.1674(3)	.3943(2)	.57478(18)	1.0(-)	.0282(11)
C(38)	.2867(3)	.3559(2)	.56916(17)	1.0(-)	.0286(11)
C(39)	.3327(3)	.3160(2)	.51139(16)	1.0(-)	.0212(10)
C(40)	.6094(3)	.20035(18)	.12925(15)	1.0(-)	.0174(9)
C(41)	.6422(3)	.26343(18)	.08031(15)	1.0(-)	.0177(9)
C(42)	.7188(3)	.23897(19)	.02319(16)	1.0(-)	.0204(9)
C(43)	.7634(3)	.15786(19)	.01381(16)	1.0(-)	.0210(9)
C(44)	.7377(3)	.09886(19)	.06779(16)	1.0(-)	.0199(9)
C(45)	.6601(3)	.11885(18)	.12697(15)	1.0(-)	.0190(9)
C(46)	.6045(3)	.35297(18)	.09087(16)	1.0(-)	.0198(9)
C(47)	.6574(3)	.3594(2)	.16075(18)	1.0(-)	.0272(11)
C(48)	.4693(3)	.3868(2)	.0957(2)	1.0(-)	.0277(11)
C(49)	.6540(3)	.4070(2)	.02873(19)	1.0(-)	.0273(11)
C(50)	.8371(3)	.1391(2)	-.05558(17)	1.0(-)	.0248(10)
C(51)	.7661(4)	.1858(2)	-.12076(18)	1.0(-)	.0311(11)
C(52)	.9526(3)	.1657(3)	-.0566(2)	1.0(-)	.0351(14)
C(53)	.8643(4)	.0484(2)	-.0611(2)	1.0(-)	.0337(11)
C(54)	.5229(3)	.04575(18)	.20837(16)	1.0(-)	.0197(9)
C(55)	.6368(3)	.05231(18)	.18369(15)	1.0(-)	.0188(9)
C(56)	.7342(3)	-.00838(19)	.21093(16)	1.0(-)	.0199(9)
C(57)	.7195(3)	-.07524(19)	.26058(16)	1.0(-)	.0227(10)
C(58)	.6019(3)	-.0811(2)	.27983(17)	1.0(-)	.0247(10)
C(59)	.5018(3)	-.02250(19)	.25557(16)	1.0(-)	.0223(10)
C(60)	.8243(3)	-.1420(2)	.29257(18)	1.0(-)	.0288(11)
C(61)	.8060(4)	-.1581(2)	.3749(2)	1.0(-)	.0354(12)
C(62)	.8298(4)	-.2204(2)	.2626(2)	1.0(-)	.0413(14)
C(63)	.9423(4)	-.1188(2)	.2741(2)	1.0(-)	.0369(12)
C(64)	.3760(3)	-.0334(2)	.27887(17)	1.0(-)	.0258(11)
C(65)	.3126(4)	.0299(2)	.3264(2)	1.0(-)	.0304(12)
C(66)	.3786(4)	-.1176(2)	.3219(2)	1.0(-)	.0397(16)
C(67)	.3033(4)	-.0247(3)	.2126(2)	1.0(-)	.0402(14)
C(68)	.3578(3)	.1891(2)	.04307(16)	1.0(-)	.0223(10)
C(69)	.4510(4)	.1582(5)	.0050(3)	1.0(-)	.135(4)
C(70)	.4449(6)	.1207(4)	-.0521(3)	1.0(-)	.110(3)
C(71)	.3488(5)	.1135(3)	-.0715(2)	1.0(-)	.073(2)
C(721)	.2671(6)	.1159(5)	-.0222(4)	0.5(-)	.034(3)<
C(722)	.2385(8)	.1922(6)	-.0537(4)	0.5(-)	.055(4)<
C(731)	.2645(6)	.1578(4)	.0353(4)	0.5(-)	.027(2)<
C(732)	.2528(7)	.2226(6)	.0080(4)	0.5(-)	.044(3)<
Residue 2.					
C(78)	.9090(5)	.5265(4)	.0303(3)	1.0(-)	.068(2)
C(79)	.8838(11)	.5992(7)	-.0078(6)	0.5(-)	.077(5)<
C(80)	.9811(7)	.6133(4)	-.0667(3)	1.0(-)	.090(3)
C(81)	.9320(8)	.4532(7)	.0693(5)	0.5(-)	.051(4)<
C(82)	.9945(10)	.4624(7)	.0273(5)	0.5(-)	.054(4)<
Residue 3.					
C(74)	.0236(4)	.0708(4)	.4655(4)	1.0(-)	.090(3)
C(75)	.0049(4)	.0594(5)	.5396(4)	1.0(-)	.100(3)
C(76)	.0192(4)	.0092(5)	.4277(4)	1.0(-)	.100(3)
C(77)	.0516(9)	.1373(5)	.4359(5)	0.5(-)	.056(3)<

table 5.1 Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for non-H atoms with e.s.d.'s in parentheses.

confirmed by the solution and the successful refinement in this space group. Reduced cell calculations did not indicate any higher metric lattice symmetry[7] and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements[8,9]. Crystal and/or instrumental instability was monitored by measurement of the intensities of three reference reflections that were collected after every 3 h of X-ray exposure time; these exhibit no significant decay during data collection. Intensity data were corrected for Lorentz and polarization effects and the scale variation, but not for absorption. Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance[10] of the three reference reflections: $\sigma^2(I) = \sigma^2(I) + (0.027I)^2$. Equivalent reflections were averaged, resulting in 10706 reflections satisfying the $I \geq 2.5\sigma(I)$ criterion of observability. The structure was solved by Patterson methods and subsequent partial structure expansion (*SHELXS86*)[11]. The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (*CRYLSQ*)[12] minimizing the function $Q = \sum_h [w(|F_o|-|F_c|)^2]$. Subsequent Fourier summations showed density which could be correlated to the disordered phenyl group (C(68)--(73)) and the two solvent molecules of toluene. Both toluene molecules were disordered over a crystallographic inversion center, each in a different way. The disorder in the phenyl group is stated by two positions with an s.o.f. (site occupancy factor) of 0.5 for C(72) and C(73). Following the inclusion of the positional parameters and appropriate s.o.f.'s of 1.0 and 0.5, respectively, of the toluene residues, the remainder of the structure refined smoothly. High thermal displacement motion was sited for the disordered fragments. The overall geometry of the toluene molecules appeared rather distorted, suggesting some degree of disorder. The hydrogen atoms of the not-disordered fragments were located in subsequent difference Fourier maps. The hydrogen of the disordered fragments were included in the final refinement riding on theircarrier atoms with their positions calculated by using sp^2 or sp^3 hybridization at the C-atom as appropriate with a fixed C-H distance of 0.96 Å. Weights were introduced in the final refinement cycles. Refinement on F_o by full-matrix least-squares techniques with

Interatomic Distances (Å)

Rh(1)-P(1)	2.1566(9)	Rh(1)-P(2)	2.1549(9)
Rh(1)-O(1)	2.070(2)	C(20)-C(21)	1.381(4)
Rh(1)-O(2)	2.074(2)	P(1) -O(3)	1.625(2)
P(1) -O(4)	1.610(2)	P(1) -O(5)	1.609(2)
P(2) -O(6)	1.612(2)	P(2) -O(7)	1.616(2)
P(2) -O(8)	1.614(2)	O(1) -C(1)	1.273(4)
O(2) -C(3)	1.264(4)	O(3) -C(6)	1.392(4)
O(4) -C(20)	1.410(3)	O(5) -C(34)	1.400(4)
O(6) -C(40)	1.412(4)	O(7) -C(54)	1.395(4)
O(8) -C(68)	1.395(4)	C(1) -C(2)	1.388(5)
C(1) -C(4)	1.508(6)	C(2) -C(3)	1.394(5)
C(3) -C(5)	1.508(7)	C(6) -C(7)	1.397(5)
C(40)-C(45)	1.387(4)	C(7) -C(21)	1.488(4)
C(45)-C(55)	1.486(4)	C(54)-C(55)	1.389(5)

Bond angles (°)

P(1)	-Rh(1)	-P(2)	99.87(3)	C(6)	-C(7)	-C(21)	123.6(3)
P(1)	-Rh(1)	-O(1)	86.43(7)	C(8)	-C(7)	-C(21)	118.0(3)
P(1)	-Rh(1)	-O(2)	172.67(7)	P(2)	-Rh(1)	-O(1)	171.94(7)
P(2)	-Rh(1)	-O(2)	84.83(7)	O(1)	-Rh(1)	-O(2)	89.41(9)
Rh(1)	-P(1)	-O(3)	119.52(8)	Rh(1)	-P(1)	-O(4)	119.18(8)
Rh(1)	-P(1)	-O(5)	110.17(9)	O(3)	-P(1)	-O(4)	103.25(11)
O(3)	-P(1)	-O(5)	97.30(11)	O(4)	-P(1)	-O(5)	104.37(11)
Rh(1)	-P(2)	-O(6)	121.07(8)	Rh(1)	-P(2)	-O(7)	117.76(9)
Rh(1)	-P(2)	-O(8)	109.76(9)	O(6)	-P(2)	-O(7)	103.23(12)
O(6)	-P(2)	-O(8)	103.80(12)	O(7)	-P(2)	-O(8)	98.04(12)
Rh(1)	-O(1)	-C(1)	125.2(2)	Rh(1)	-O(2)	-C(3)	125.3(2)
P(1)	-O(3)	-C(6)	126.46(19)	P(1)	-O(4)	-C(20)	120.07(17)
P(1)	-O(5)	-C(34)	129.79(19)	O(4)	-C(20)	-C(21)	117.4(2)
P(2)	-O(6)	-C(40)	118.72(19)	O(4)	-C(20)	-C(25)	119.1(3)
P(2)	-O(7)	-C(54)	128.0(2)	P(2)	-O(8)	-C(68)	130.8(2)
C(7)	-C(21)	-C(20)	122.9(3)	O(1)	-C(1)	-C(2)	126.6(3)
C(7)	-C(21)	-C(22)	118.8(3)	O(1)	-C(1)	-C(4)	115.2(3)
O(2)	-C(3)	-C(2)	126.6(3)	O(2)	-C(3)	-C(5)	115.9(3)
O(3)	-C(6)	-C(7)	118.3(3)	O(3)	-C(6)	-C(11)	119.5(3)
O(7)	-C(54)	-C(55)	118.8(3)	O(7)	-C(54)	-C(59)	118.6(3)
C(45)	-C(55)	-C(54)	123.0(3)	C(45)	-C(55)	-C(56)	118.3(3)
O(5)	-C(34)	-C(35)	118.7(3)	O(5)	-C(34)	-C(39)	120.0(3)
O(6)	-C(40)	-C(41)	119.4(3)	O(6)	-C(40)	-C(45)	117.4(3)
C(40)	-C(45)	-C(55)	123.4(3)	C(44)	-C(45)	-C(55)	118.8(3)
O(8)	-C(68)	-C(69)	123.4(4)	O(8)	-C(68)	-C(731)	123.1(4)
O(8)	-C(68)	-C(732)	109.2(5)	C(2)	-C(1)	-C(4)	118.2(3)
C(1)	-C(2)	-C(3)	126.3(3)	C(2)	-C(3)	-C(5)	117.5(4)

table 5.2 Selected data on the geometry. E.s.d.'s are given in parentheses.

Torsion angles (°)*

P(2)	-Rh(1)-P(1)	-O(3)	117.84(9)	O(3)	-C(6)	-C(7)	-C(21)	-.5(4)
P(2)	-Rh(1)-P(1)	-O(5)	-130.85(9)	C(11)	-C(6)	-C(7)	-C(8)	-5.1(4)
O(1)	-Rh(1)-P(1)	-O(3)	-57.10(11)	C(11)	-C(6)	-C(7)	-C(21)	173.7(3)
O(1)	-Rh(1)-P(1)	-O(4)	174.74(11)	O(3)	-C(6)	-C(11)	-C(10)	179.7(3)
O(1)	-Rh(1)-P(1)	-O(5)	54.21(11)	O(3)	-C(6)	-C(11)	-C(16)	.3(4)
P(1)	-Rh(1)-P(2)	-O(6)	-9.44(10)	C(6)	-C(7)	-C(21)	-C(20)	50.8(4)
P(1)	-Rh(1)-P(2)	-O(7)	118.81(10)	C(6)	-C(7)	-C(21)	-C(22)	-133.6(3)
P(1)	-Rh(1)-P(2)	-O(8)	-130.27(10)	C(8)	-C(7)	-C(21)	-C(20)	-130.4(3)
O(2)	-Rh(1)-P(2)	-O(6)	176.23(11)	C(21)	-C(20)	-O(4)	-P(1)	-70.8(3)
O(2)	-Rh(1)-P(2)	-O(7)	-55.52(12)	C(25)	-C(20)	-O(4)	-P(1)	112.4(3)
O(2)	-Rh(1)-P(2)	-O(8)	55.40(11)	O(4)	-C(20)	-C(21)	-C(7)	-6.2(4)
P(1)	-Rh(1)-O(1)	-C(1)	-176.5(3)	O(4)	-C(20)	-C(21)	-C(22)	178.1(2)
O(2)	-Rh(1)-O(1)	-C(1)	-2.5(3)	O(4)	-C(20)	-C(25)	-C(24)	-178.1(3)
P(2)	-Rh(1)-O(2)	-C(3)	-179.0(3)	O(4)	-C(20)	-C(25)	-C(30)	7.4(4)
O(1)	-Rh(1)-O(2)	-C(3)	-4.6(3)	C(35)	-C(34)	-O(5)	-P(1)	81.5(4)
Rh(1)	-P(1)	-O(3)	-C(6)	-104.0(2)	C(39)	-C(34)	-O(5)	-P(1)	-102.4(3)
O(4)	-P(1)	-O(3)	-C(6)	31.2(2)	C(41)	-C(40)	-O(6)	-P(2)	110.2(3)
O(5)	-P(1)	-O(3)	-C(6)	137.8(2)	C(45)	-C(40)	-O(6)	-P(2)	-71.2(3)
Rh(1)	-P(1)	-O(4)	-C(20)	-168.32(17)	O(6)	-C(40)	-C(41)	-C(42)	-173.6(3)
O(3)	-P(1)	-O(4)	-C(20)	56.3(2)	O(6)	-C(40)	-C(41)	-C(46)	10.6(5)
O(5)	-P(1)	-O(4)	-C(20)	-44.9(2)	O(6)	-C(40)	-C(45)	-C(44)	173.8(3)
Rh(1)	-P(1)	-O(5)	-C(34)	-127.9(3)	O(6)	-C(40)	-C(45)	-C(55)	-6.4(5)
O(3)	-P(1)	-O(5)	-C(34)	-2.7(3)	C(40)	-C(45)	-C(55)	-C(54)	50.9(5)
O(4)	-P(1)	-O(5)	-C(34)	103.0(3)	C(40)	-C(45)	-C(55)	-C(56)	-132.1(3)
Rh(1)	-P(2)	-O(6)	-C(40)	-167.26(17)	C(44)	-C(45)	-C(55)	-C(54)	-129.3(3)
O(7)	-P(2)	-O(6)	-C(40)	58.3(2)	C(44)	-C(45)	-C(55)	-C(56)	47.7(4)
O(8)	-P(2)	-O(6)	-C(40)	-43.6(2)	C(55)	-C(54)	-O(7)	-P(2)	-59.7(4)
Rh(1)	-P(2)	-O(7)	-C(54)	-108.5(2)	C(59)	-C(54)	-O(7)	-P(2)	126.7(3)
O(6)	-P(2)	-O(7)	-C(54)	27.8(3)	O(7)	-C(54)	-C(55)	-C(45)	-1.2(4)
O(8)	-P(2)	-O(7)	-C(54)	134.1(2)	O(7)	-C(54)	-C(55)	-C(56)	-178.2(3)
Rh(1)	-P(2)	-O(8)	-C(68)	-121.4(3)	C(59)	-C(54)	-C(55)	-C(45)	172.2(3)
O(6)	-P(2)	-O(8)	-C(68)	107.9(3)	C(59)	-C(54)	-C(55)	-C(56)	-4.8(5)
O(7)	-P(2)	-O(8)	-C(68)	2.0(3)	O(7)	-C(54)	-C(59)	-C(58)	177.3(3)
C(2)	-C(1)	-O(1)	-Rh(1)	7.4(5)	O(7)	-C(54)	-C(59)	-C(64)	-1.9(4)
C(4)	-C(1)	-O(1)	-Rh(1)	-172.6(2)	C(45)	-C(55)	-C(56)	-C(57)	-175.8(3)
O(1)	-C(1)	-C(2)	-C(3)	-5.4(6)	C(69)	-C(68)	-O(8)	-P(2)	-82.6(5)
C(4)	-C(1)	-C(2)	-C(3)	174.5(4)	C(731	-C(68)	-O(8)	-P(2)	80.5(5)
C(1)	-C(2)	-C(3)	-O(2)	-3.1(6)	C(732	-C(68)	-O(8)	-P(2)	132.8(4)
C(1)	-C(2)	-C(3)	-C(5)	178.9(4)	O(8)	-C(68)	-C(69)	-C(70)	-175.5(5)
C(2)	-C(3)	-O(2)	-Rh(1)	7.8(5)	O(8)	-C(68)	-C(731)	-C(721)	179.2(5)
C(5)	-C(3)	-O(2)	-Rh(1)	-174.2(3)	O(8)	-C(68)	-C(731)	-C(722)	130.4(5)
C(7)	-C(6)	-O(3)	-P(1)	-62.1(3)	O(8)	-C(68)	-C(731)	-C(732)	86.9(6)
C(11)	-C(6)	-O(3)	-P(1)	123.6(3)	O(8)	-C(68)	-C(732)	-C(722)	173.8(7)
O(3)	-C(6)	-C(7)	-C(8)	-179.3(3)	O(8)	-C(68)	-C(732)	-C(731)	-117.7(6)

* The sign of the torsion angle is positive if, when looking from atom-2 to atom-3, a clockwise motion of atom-1 would superimpose it on atom-4.

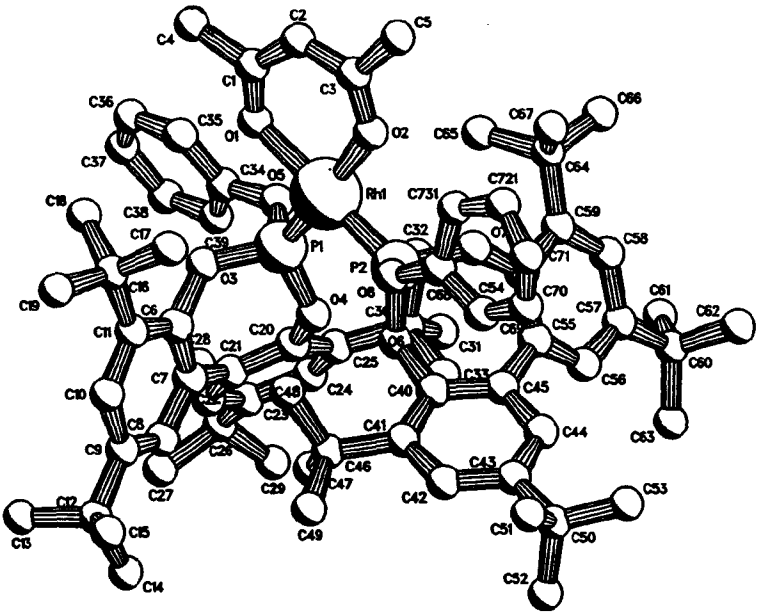


fig.5.1 PLUTO drawing of the molecule of the title compound illustrating the puckering and the adopted numbering scheme. H-atoms have been omitted to improve clarity.

anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for the hydrogen atoms converged at R_F = 0.042 (wR = 0.046). The crystal exhibited some secondary extinction for which the F values were corrected by refinement of an empirical isotropic extinction parameter[13]. A final difference Fourier map was essentially featureless with the highest peaks in the vicinity of the disordered fragments. The final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for the non-hydrogen atoms are given in Table 5.1. Molecular geometry data are collected in Table 5.2. Tables of hydrogen atom positions, thermal displacement parameters, comprehensive lists of bond distances and angles and tables of (F_o), (F_c) and $\sigma(F)$ are given as supplementary material[1] for this paper. Scattering factors were taken from Cromer & Mann[14]. Anomalous dispersion factors taken from Cromer & Liberman[15] were included in F_c. All calculations were carried out on the CDC-Cyber 962-31computer of the University of Groning-

en with the program packages *XTAL*[16], *PLATON*[17] (calculation of geometric data) and a locally modified version of the program *PLUTO*[18] (preparation of illustrations).

5.3 Results and discussion.

The identification of the atoms and the configuration are shown in the *PLUTO* drawing of Fig. 5.1.; the packing of the molecules is shown in the unit cell in Fig. 5.2. Each asymmetric unit contains one complete molecule of the title compound with no atom setting at special position and two half molecules of disordered toluene solvent molecules. The triclinic unit cell contains two discrete molecules (Fig. 5.2) of the title compound and two toluene molecules separated by normal van der Waals distances. Both toluene molecules possess a crystallographic imposed center of inversion. The square planar structure of the complex (1) is tetrahedrical distorted (distances of atoms from root mean square (r.m.s.) plane of P(1)-P(2)-O(2)-O(1).; P(1) = -0.096(7), P(2)

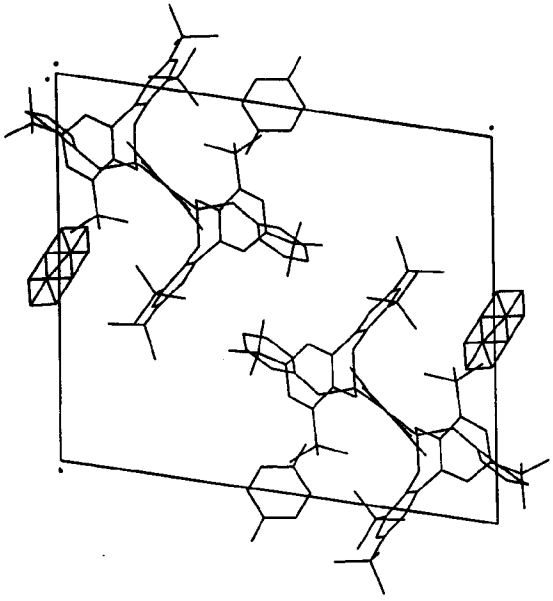


fig.5.2 Molecular packing viewed down a-axis with the title compound and the disordered toluene molecule; hydrogen atom bonds omitted for the sake of clarity.

= 0.096(6), O(1) = 0.108(7), O(2) = -0.110(6) Å). The central rhodium atom is in the plane (distance r.m.s. plane-Rh = 0.004(6) Å). Sterical hindrance of the two phosphite groups is demonstrated by the large P(1)-Rh-P(2) angle of 99.87(3)°, vs 94.8(2)° for the triphenylphosphite rhodiumcomplex (2)[2] The O(1)-Rh-O(2) angle (89.41(2)°) is only slightly larger then that of the triphenylphosphite analogue (2) (88.8(2)°). The sterical hindrance has led to distortions within the phosphite ligands. The different P-O-C angles within the ligands (P(1)-O(3)-C(6) = 126.4(2)° vs P(1)-O(4)-C(20) = 120.1(2)° and P(2)-O(6)-C(40) = 118.7(2)° vs P(2)-O(7)-C(54) = 128.0(2)°) are examples of this distortion. The angles between the two bridged phenyl-groups of the phosphite ligands are 49.7(2) and 51.5(2)° respectively. The cone angle[19] for the 2,2'-bis(4,6-di-t-butylphenyl)phenyl phosphite calculated from this X-ray structure is 164°. The high π-acidity of arylphosphites leads to the formation of strong π-coordination bonds, which might explain the formation of the bis-phosphite complex (1), even though the cone angle of the ligand is too large to expect the formation of bisphosphite rhodium complexes. (Triphenylphosphine, cone angle 145°, exclusively yields monophosphine complexes when reacted with $Rh(acac)(CO)_2$, even when a large excess of phosphine is used[20].

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